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ULTRAFINE PARTICLE PRODUCTION METHOD

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[There are no amendments to this patent.]

Claims

1. An ultrafine particle production method in which niobium halogenide and sodium react with each other while in vapor phases.
2. The ultrafine particle production method described in Claim 1, in which the reaction takes place at a temperature equal to or lower than the boiling point of the sodium halogenide created as a by-product.

3. The ultrafine particle production method described in Claims 1 and 2, in which the niobium halogenide is introduced into a reaction chamber at a high linear velocity.

4. The ultrafine particle production method described in Claim 3, in which the niobium halogenide is introduced into the reaction chamber at a linear velocity equal to or higher than 1 m/sec.

#### Detailed explanation of the invention

##### Industrial application field

The present invention pertains to an ultrafine particle production method in which niobium halogenide and sodium (will be referred to as Na, hereinafter) react with each other while in vapor phases in order to produce ultrafine metallic niobium particles efficiently. The ultrafine particle used here refers to a powdery body with a grain size equal to or smaller than 1  $\mu\text{m}$ . Because ultrafine powdery bodies demonstrate completely different characteristics from those demonstrated by their bulk state due to their fineness, new applications are expected.

An atomizing method and a gas evaporation method are known as physical methods for producing metallic ultrafine particles; and a thermal cracking method, a gaseous reduction method, and a gas-phase reaction method are known as chemical methods. The gas-phase reaction method is a method in which fine powdery bodies are obtained by reducing the vapor of a metal chloride using  $\text{H}_2$  or CO. While this method was able to be used for continuous operation, the reducing power of  $\text{H}_2$  or CO was weak, resulting in a shortcoming that substances which could be made into ultrafine powders were limited. In addition, with this method, the reaction temperature also needed to be relatively high.

In addition, in the case of the gas evaporation method, when a high-melting-point metal (Nb, Ta, Mo, W, etc.) with a low vapor pressure was used, the production of ultrafine particles was difficult to achieve.

In general, it is necessary to increase the nucleation rate by attaining a high supersaturation ratio (actual vapor pressure/equilibrium vapor pressure) in order to obtain ultrafine particles using the gas evaporation method. The reduction reaction between the halogenide and sodium in the present invention can be expressed by the following formula.

$$\text{NbX}_5 + 5\text{Na} \rightarrow \text{Nb} + 5\text{NaX} \quad (\text{X} = \text{halogen}) \dots (1)$$

(g)      (g)      (s)

The products of the gas-phase reaction method are all solids. Therefore, a wide temperature range is realized, so that a high supersaturation ratio can be attained stably with a strong reducing power, and because Na with a relatively high vapor pressure is used, the reaction rate is high also.

In addition, device factors, such as reactor structure, reaction gas introduction method, and heating method, significantly affect the production of the ultrafine particles.

The present inventors conducted studies in search of a method for obtaining niobium ultrafine particles efficiently in consideration of the aforementioned points and completed the present invention as a result.

The present invention will be described in detail next. Niobium halogenide and Na are made to react with each other in an inert gas so as to vaporize them, and the Na vapor and then the niobium halogenide vapor are sent at high linear velocities into a reaction chamber maintained at a prescribed reaction temperature. Niobium chloride (will be referred to as  $\text{NbCl}_5$ , hereinafter), niobium bromide (will be referred to as  $\text{NbBr}_5$ , hereinafter), niobium iodide (will be referred to as  $\text{NbI}_5$ , hereinafter), niobium fluoride (will be referred to as  $\text{NbF}_5$ , hereinafter), or a lower halogenide of such may be used for the niobium halogenide used here in order to obtain metallic niobium with a grain size of  $1\text{ }\mu\text{m}$  or smaller.

Next, the present invention will be explained in detail based on an example in which  $\text{NbCl}_5$  is used. As shown in formula (1), the appropriate ratio between the quantities of  $\text{NbCl}_5$  and Na is 1:5 in terms of molar ratio. In the present invention, too, there is no problem as long as the equivalent weight is maintained. However, it is preferable that the reaction takes place in the range of 0.5-2.0 equivalent weight, or preferably, at 0.8-1.2 equivalent weight. The reason is that  $\text{NbCl}_5$  loss increases when the equivalent weight is equal to or lower than 0.8, and that not only is it uneconomical, but also treatment of excessive Na becomes complicated when the equivalent weight is equal to or greater than 1.2.

Because the reaction begins to take place at  $300^\circ\text{C}$  or higher, there is no problem as long as the reaction temperature is  $300^\circ\text{C}$  or higher, and it is preferable that the upper temperature limit be equal to or lower than the boiling point of  $\text{NaCl}$ , that is,  $1400^\circ\text{C}$ , in order to increase the nucleation rate. It is particularly desirable that [the upper temperature limit] be equal to or lower than its melting point, that is,  $800^\circ\text{C}$ . Particles with a uniform grain size can be obtained when the reaction takes place at a temperature equal to or lower than the aforementioned melting point.

It is desirable that the vaporized  $\text{NbCl}_5$  be kept at a temperature equal to or higher than the melting point and introduced at a high velocity into the reaction chamber where the Na vapor has already been introduced.

Blowing into the reaction chamber should be done at a high linear velocity in order to obtain ultrafine powdery products. Although there is no special restriction as long as it is equal to or higher than  $1\text{ m/sec}$ ,  $3\text{ m/sec}$  is preferable due to a restriction imposed by the length of the reaction chamber.

Although the reaction is usually carried out under atmospheric pressure, it can be carried out under a reduced pressure or an increased pressure if the device permits.

Although there is no special temperature requirement during the capturing of the products, namely, the ultrafine niobium powders created, the by-product NaCl and the excessive Na may be kept at a temperature equal to or higher than 100°C and captured while separating the Na, or they may be captured after being cooled to a temperature equal to or lower than 0°C.

It is convenient to remove the Na and the NaCl from the products captured using an organic solvent containing no water. After the wash, the ultrafine particles to which the organic solvent are adhered can be stabilized by forming an oxide film on the surfaces of said ultrafine particles by drying them in a 50°C or lower oxygen-containing inert gas or in a dry air.

With the present invention, 0.05-0.2- $\mu$ m metallic niobium can be obtained at a high yield.

In addition, because the reaction takes place at a relatively low temperature and instantaneously, [the particles] can be produced quite efficiently.

Furthermore, because the reducing agent, that is, sodium, is relatively cheap, it is more economical.

The present invention will be explained in further detail using application examples.

#### Application Example 1

600 g of 99.9% pure NbCl<sub>5</sub> obtained by chlorinating commercially available ferro niobium and removing impurities using a conventional method were put in a NbCl<sub>5</sub> hopper.

Commercially available Na was kept at 760°C using a vaporizer, and Ar gas was introduced from the top as a carrier at the rate of 11 L/min into a vertical reaction chamber in which Na vapor (Na 5 g/min) was kept at 800°C. On the other hand, NbCl<sub>5</sub> was sent from the hopper at the rate of 10 g/min into a vaporization chamber kept at 300°C by screws so as to vaporize it, and NbCl<sub>5</sub> was introduced at the linear velocity of 1 m/sec using the 1 L/min Ar into the reaction chamber through a nozzle.

The ratio of the Na was equivalent to 1.2 times that of the NbCl<sub>5</sub>. The mixture of ultrafine Nb powder, sodium, and sodium chloride led into a collector from an exit provided at the bottom of the reaction chamber was removed while it was still in the collector after the reaction was completed, 1 L ethyl alcohol was added to it so as to dissolve the Na, and the ethyl alcohol was removed by means of sedimentation. 9 L ethylene glycol were added to the slurry obtained then so as to dissolve the NaCl, and the ultrafine niobium powders were washed using ethyl alcohol so as to separate them by means of sedimentation.

As for the ultrafine powder slurry in the ethyl alcohol, the ethyl alcohol was evaporated in room-temperature dry air in order to stabilize the surfaces of the ultrafine powders by means of oxidation.

The ultrafine niobium powders obtained are described as follows.

Yield	180 g (yield of 87%)
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Grain size	0.05-0.1 $\mu\text{m}$
Nb	94.4%
O	5.6%
Cl	0.1%

An electron micrograph (x 50,000) of the ultrafine niobium powders is shown in Figure 1.

#### Application Example 2

$\text{NbBr}_5$  and Na were made to react with each other using the device used in Application Example 1.

The  $\text{NbBr}_5$  was vaporized at a rate of 8.3 g/min and spouted into the reaction chamber through the nozzle. At the same time, Na vapor was put through the reaction chamber kept at 600°C at a rate of 2 g/min. The Ar gas as a carrier was used at the rates of 2 L/min and 1.5 L/min, respectively.

1.5 L 2-aminoethanol and 3 L ethanol were used to remove the Na and the NaBr and stabilize the ultrafine powders created.

Yield	90%	85 g
Nb	92%	
O	8%	
Br	n.d.	
Grain size	0.2 $\mu\text{m}$	

An electron micrograph (x 10,000) of the ultrafine niobium powder is shown in Figure 2.

#### Brief description of the figures

Figure 1 shows an electron micrograph (x 50,000) of the ultrafine particles obtained through the reaction of  $\text{NbCl}_5$  and Na.

Figure 2 shows an electron micrograph (x 10,000) of the ultrafine particles obtained through the reaction of  $\text{NbBr}_5$  and Na.



Figure 1

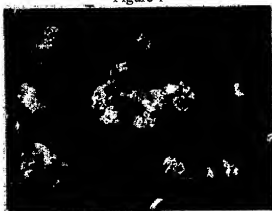


Figure 2